

IMPACT OF USE ON RELEASE PROCESSES IN AUSTENITIC STEEL TP347HFG

WPŁYW EKSPLOATACJI NA PROCESY WYDZIELENIOWE W AUSTENITYCZNEJ STALI TP347HFG

The article presents an analysis of precipitation processes in heat-resistant TP347HFG steel after 41,000 h of operation at 585°C. Microstructure investigation showed that the use of the tested steel resulted mainly in the precipitation processes occurring at grain boundaries. Identification of the precipitates showed the presence of $M_{23}C_6$ carbides and σ phase particles along boundaries. Single $M_{23}C_6$ carbide particles were revealed also at twin boundaries. Inside austenite grains, apart from large, primary precipitates, finely-dispersed secondary NbX particles ($X = C, N$) were also observed.

Keywords: steels for the power industry, TP347HFG, microstructure, precipitation processes, mechanical properties, service life

W pracy przedstawiono analizę procesów wydzieleniowych w żarowytrzymałej stali TP347HFG po 41 000 h eksploatacji w temperaturze 585°C. Przeprowadzone badania mikrostrukturalne wykazały, że eksploatacja badanej stali spowodowała przede wszystkim zajście procesów wydzieleniowych na granicach ziaren. Identyfikacja wydzieleni wykazała występowanie po granicach węglików typu $M_{23}C_6$ oraz cząstek fazy σ . Pojedyncze cząstki węglików $M_{23}C_6$ ujawniono również na granicach bliźniaków. Wewnątrz ziaren austenitu oprócz dużych, pierwotnych wydzieleni, obserwowano również drobnodyspersyjne wtórne cząstki NbX ($X = C, N$).

Słowa kluczowe: stale dla energetyki, TP347HFG, mikrostruktura, procesy wydzieleniowe, właściwości mechaniczne, trwałość eksploatacyjna

1. INTRODUCTION

Progressively more restrictive European Union regulations in the field of environmental protection require the power industry to strive to increase the efficiency of units in order to reduce the emission of pollutants into the atmosphere. The increase in the efficiency of units is related, among others, to increased temperature and steam pressure parameters. This forces the use of new construction materials in modern and modernised units of higher and higher heat resistance, e.g. heat-resistant austenitic steels. These materials are mainly used for steam superheater coils that can operate at temperatures above 600°C [1, 2]. The following grades of austenitic steels are used in modern power units: TP347HFG, Super 304H and HR3C.

TP34HFG steel belongs to stabilised austenitic steels of the 19/11 group. This steel was created as a result of modification of the thermo-mechanical treatment of the coarse-grained TP347H steel. This modification made it possible

to obtain steel with a fine-grained structure, which significantly improved the resistance to corrosion and oxidation of this material. The increase in corrosion and oxidation resistance of the fine-grained TP347HFG steel was obtained with a slightly lower creep strength compared to the coarse-grained TP347H steel [3].

Precipitation strengthening in steels for operation at elevated temperatures plays an important role in increasing the functional properties and stabilising the microstructure. In austenitic steels, the particles of the second phase play an important role in increasing the strength properties and creep resistance. Precipitation strengthening in austenitic steels can be realised both through MX precipitates (with the structure of sodium chloride), ϵ -Cu, phase Z (NbCrN) and, in the initial stage of operation, through $M_{23}C_6$ carbides. At the same time, precipitation processes in austenitic steels are the dominant process influencing the degradation of the microstructure and properties [1, 2, 4–6]. Hence, forecasting the durability and safe operation

time of devices made of these materials and operated in real working conditions is mainly related to the analysis of the advancement of separation processes. This type of research is carried out not only in laboratory conditions (simulations), but also on sections taken from the components after use. The data obtained in this way make it possible to build a knowledge base and develop material characteristics used in engineering practice to assess the degree of wear of the structure of a given material. In practice, this translates into an extension of the time of safe operation of power unit machine and device components. The article presents the results of analysis of precipitation processes in TP347HFG steel after operation at 585°C.

2. MATERIAL AND METHODOLOGY

The test material was TP347HFG creep resistant austenitic steel with the following chemical composition (weight %): 0.08C; 0.43Si; 1.89Mn; 0.017P; 0.003S; 18.45Cr; 12.08Ni; 0.61Nb; 0.05N. The tested material was collected from a section of a steam superheater coil pipeline after over 41,000 hours of operation at 585°C.

The scope of the research included: chemical composition analysis, microstructure studies using a scanning electron microscope and a transmission electron microscope, and the identification of precipitates using selective electron diffraction. The chemical composition analysis was performed using a SpectroLab spark spectrometer. The microstructure investigation was carried out on a metallographic microsection etched with the Mi19Fe reagent using a Jeol 6610LV scanning electron microscope (SEM). Transmission electron microscope studies were performed with the use of thin foils with a TITAN 80-300 (TEM) microscope. The thin foils were prepared as disks with a diameter of 3 mm and a thickness of approximately 100 µm. The etching was carried out electrolytically in a 20% perchloric acid solution in ethanol at -30°C. The identification of the precipitates was carried out using selective electron diffraction.

3. TEST RESULTS AND OVERVIEW

On delivery, i.e. after solution heat treatment, heat-resistant austenitic steels are characterised by austenitic structure with annealing twins and, in the case of stabi-

lised steels, also by relatively numerous and large primary precipitates. The use of austenitic steels leads mainly to precipitation processes both at grain boundaries and inside the grains [4, 5].

After use, the tested steel was characterised by an austenitic matrix with numerous precipitates of different morphology at grain boundaries and inside the grains (Fig. 1). Single particles were also observed at the borders of the twins (shown by the red arrows). The grain size of the tested steel was 9–7 according to the ASTM scale, which corresponds to the average grain diameter of 15.6–31.2 µm.

There were $M_{23}C_6$ chromium-rich carbides at grain boundaries and twin boundaries (Fig. 2). Precipitation of $M_{23}C_6$ carbides in austenitic steels is a natural process, mainly related to the solubility of carbon in the matrix, limited with temperature [4–6]. In austenitic steels, $M_{23}C_6$ carbides are first released at the boundaries of the austenite grains, and then at the boundaries of the twins [6]. The slower precipitation processes occurring at the twins' borders are due to their lower energy compared to high-angle borders (3–10% of the energy of a large angle) [6, 7]. Precipitation processes at the borders are also related to their nature. The preferred boundaries at which the $M_{23}C_6$ carbide precipitation occurs are the boundaries characterised by a high degree of coincidence or boundaries with a large disorientation angle [7, 8]. In the initial stage of operation, $M_{23}C_6$ dispersion particles have a positive effect on the properties of austenitic steels, increasing creep resistance by hindering the slip along grain boundaries [6, 9]. However, the high tendency of these precipitates to coagulate leads to an increase in the size of these particles and, consequently, to the reduction of this beneficial effect [5].

At grain boundaries, as energetically privileged areas for nucleation and growth of precipitates, apart from $M_{23}C_6$ carbides, characteristic σ phase particles were revealed (indicated by black arrows in Fig. 1, Fig. 3).

σ phase precipitates are rich mainly in iron and chromium [4, 6]. The preferred place for the σ phase particle precipitation is the junction of the three grain boundaries (Fig. 1 – indicated by white arrows). The precipitation of the σ phase may occur as a result of the disintegration of ferrite d , independent nucleation or as a result of the in situ transformation of $M_{23}C_6$ carbides [5, 6, 9]. The rate of the σ phase precipitation and growth process depends mainly on the chemical composition, i.e. the content of chromium and silicon [6, 9, 10]. The above is also influenced by the

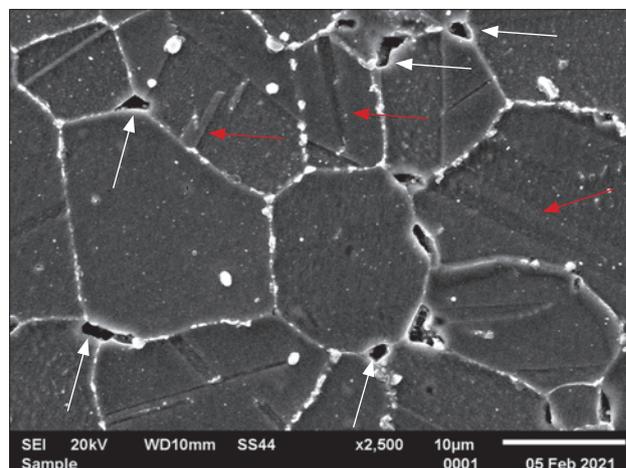
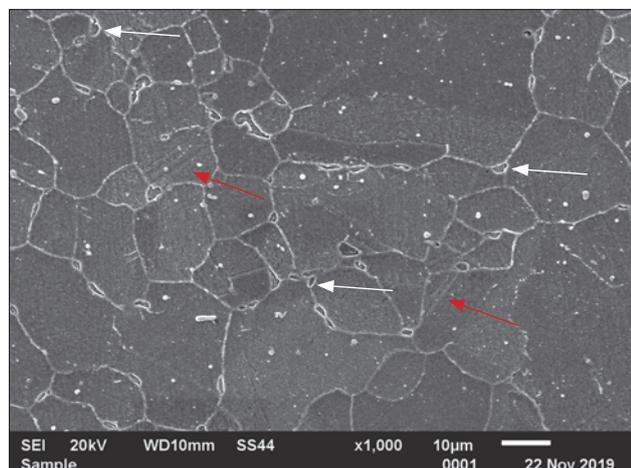


Fig. 1. Microstructure of the tested steel after use, SEM

Rys. 1. Mikrostruktura badanej stali po eksploatacji, SEM

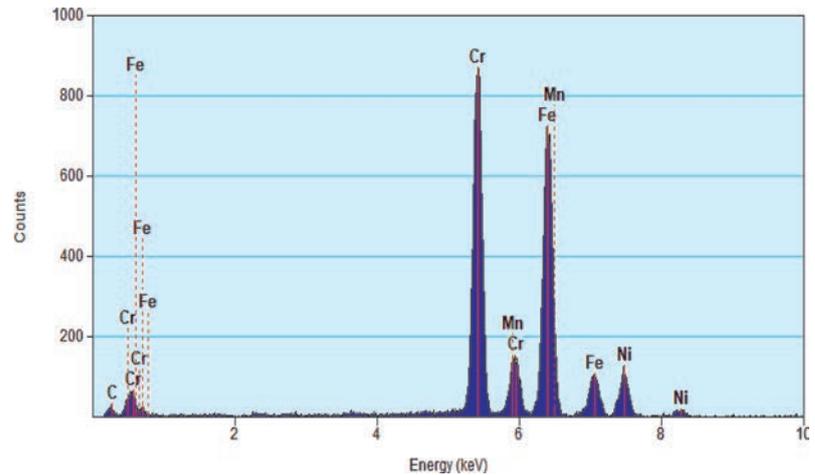
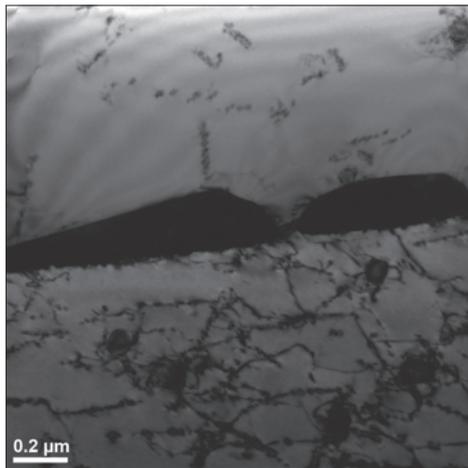


Fig. 2. $M_{23}C_6$ carbides precipitated at grain boundary a), $M_{23}C_6$ carbide EDS spectrum indicated with an arrow (b), TEM
Rys. 2. Węgliki $M_{23}C_6$ wydzielone na granicy ziarna (a), widmo EDS węglika $M_{23}C_6$ wskazanego strzałką (b), TEM

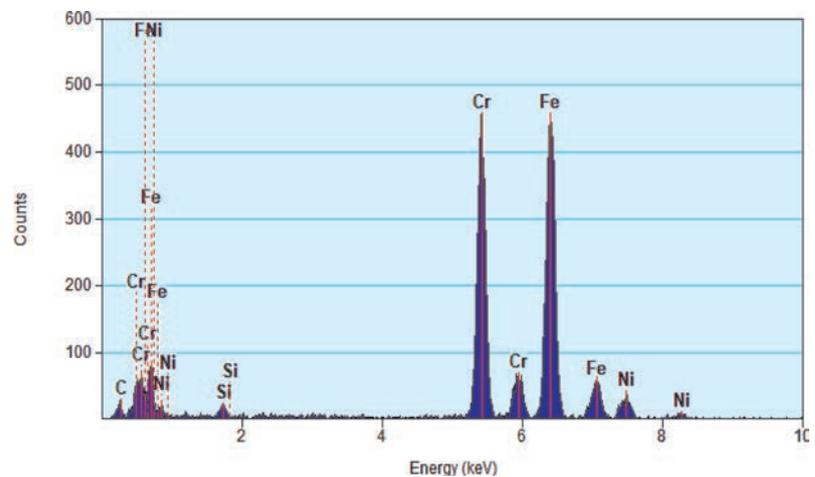
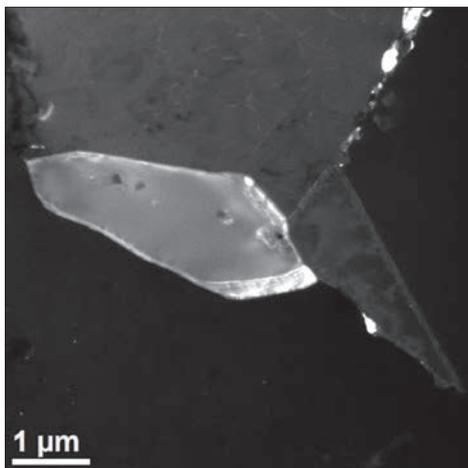


Fig. 3. Precipitate of the σ phase at the contact point of the three grain boundaries in the tested steel (a); EDS spectrum of phase σ (b), TEM
Rys. 3. Wydzielenie fazy σ na styku trzech granic ziaren w badanej stali (a); widmo EDS fazy σ (b), TEM

content of carbide-forming elements, e.g. niobium, which binds carbon and/or nitrogen atoms, thus increasing the activity of chromium atoms [5, 6].

The precipitation of chromium-rich particles at grain boundaries – $M_{23}C_6$ carbides and the σ phase – locally in the form of a continuous grid, not only leads to a decrease in mechanical properties (decrease in plasticity and ductility of steel and an increase in brittleness), but also may be the cause of an increase in the susceptibility of austenitic steel to intercrystalline corrosion [4, 5, 11, 12]. This may cause individual grains to ‘fall out’ during the preparation of the microsection – etching, as was observed in the HR3C steel [11]. Fine $M_{23}C_6$ carbides separated at grain boundaries have a positive effect on creep resistance by hindering the sliding along the boundaries. The increase in the size of these precipitates causes the disappearance of this beneficial effect [6, 9]. The influence of the sigma phase on creep resistance is ambiguous. The research part indicates its positive effect, while other researchers indicate its negative role [6, 9, 10].

The TP347HFG steel belongs to the group of stabilised austenitic steels, i.e. in their chemical composition, they contain a strongly carbide-forming element (in this case niobium) with a higher affinity to carbon than chromium.

This results in the appearance of large, primary NbX carbides already in the delivery condition (Figs. 1, 4). These precipitates in the structure of austenitic steels appear in the last stage of crystallisation, therefore they are often observed near or at grain boundaries (Fig. 4). The main task of the primary NbX precipitates is to bind carbon atoms, which is to prevent or reduce the tendency to precipitate $M_{23}C_6$ carbides at grain boundaries [6, 13, 14]. Due to their dimensions, the primary NbX precipitates do not significantly affect the strengthening of austenitic steels by the precipitation mechanism [13, 15]. According to [14], the primary NbX precipitates should be treated as unfavourable, because during operation nucleation and growth of creep voids may occur at their matrix/particle interface.

During the use of the tested steel, apart from the primary precipitates, also secondary particles Nb(C,N) were revealed inside the grains (Fig. 5). These particles nucleate mainly on dislocation, but they are also observed in misalignments [6]. The calculated average diameter of secondary NbX precipitates was $53 \text{ nm} \pm 15 \text{ nm}$. Due to their dispersive form, these precipitates are effective obstacles to the movement of dislocations, inhibiting or limiting their ability to move freely (Fig. 2). The stress needed to bypass the particle with Orowan mechanism is approxi-

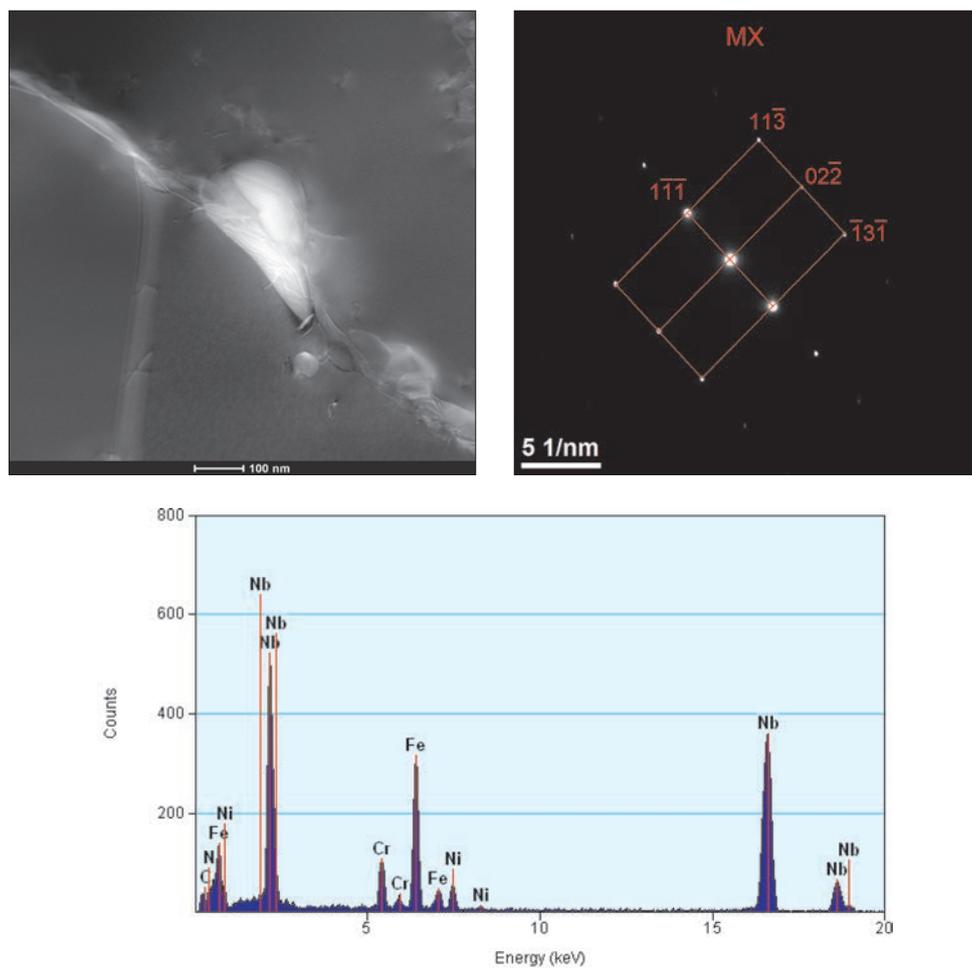


Fig. 4. Primary NbX precipitate near grain boundary (a); solved diffraction (b); EDX spectrum of a precipitate (c), TEM
Rys. 4. Wydzielenie pierwotne NbX w pobliżu granicy ziarna (a); rozwiązana dyfrakcja (b); widmo EDX wydzielenia (c), TEM

mately 27 MPa for the NbX secondary precipitates, while for $M_{23}C_6$ carbides it is only 10 MPa [15]. This indicates the dominant role of this precipitate as a precipitate responsible for the significant strengthening of austenitic steel by the precipitation mechanism. This is confirmed by the calculations presented in [13], according to which the sec-

ondary releases of NbX contribute to approx. 30% increase of yield strength in TP347HFG steel. An equally important issue from the point of view of long-term operation of austenitic steels is the low tendency to coagulate NbX precipitates, which translates into the stability or slow reduction of strength properties over time [4, 5, 13].

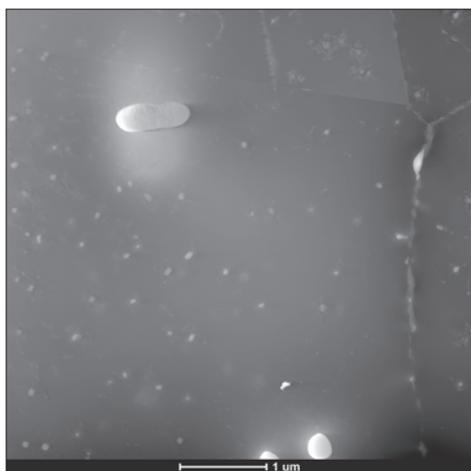


Fig. 5. Dispersed and large NbX particles precipitated inside the grains, TEM

Rys. 5. Dyspersyjne i duże cząstki NbX wydzielone wewnątrz ziaren, TEM

4. SUMMARY

The TP347HFG austenitic steel was tested after over 41,000 hours of operation at 585°C. After use, the tested steel was characterised by a fine-grained structure with numerous precipitates and twins. In the tested steel, precipitation processes were observed at grain boundaries, twin boundaries and inside grains. $M_{23}C_6$ carbides and sigma phase precipitates were revealed at grain boundaries. Single $M_{23}C_6$ precipitates were observed also at twin boundaries. NbX dispersive secondary particles are also disclosed inside the grains, in addition to large primary precipitates. At the initial stage of operation, the precipitation of secondary phases has a positive effect on the increase in the strength of the tested steel by the precipitation mechanism. The increase in the size of secondary precipitates and the release of the unfavourable sigma phase and its coagulation during long-term operation contribute to the process of microstructure degradation, which has a significant impact on the performance and durability of the material.

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